

Application No. 10/628,373
Amendment dated October 19, 2005
After Final Office Action of August 19, 2005

Docket No.: 20435-00141-US

LISTING OF CLAIMS

1. (Currently amended). A liquid oligomeric composition comprising:
a multifunctional mercaptan;
an organic soluble, ungelled, uncrosslinked, Michael addition product having a plurality of pendant unsaturated acrylate groups; and
the substantial total absence of exogenous photoinitiator.
2. (Previously presented). The liquid oligomeric composition, according to claim 1, wherein said Michael addition product is formed from a multifunctional acrylate Michael acceptor and a β -dicarbonyl Michael donor.
3. (Previously presented). The liquid oligomeric composition, according to claim 2, wherein said β -dicarbonyl Michael donor is selected from the group consisting of β -keto esters, β -diketones, β -ketoamides, β -ketoanilides, and mixtures thereof.
4. (Previously presented). The liquid oligomeric composition, according to claim 2, wherein said multifunctional acrylate Michael acceptor is selected from the group consisting of diacrylates, triacrylates, and tetraacrylates.
5. (Previously presented). The liquid oligomeric composition, according to claim 2, wherein said β -dicarbonyl Michael donor is a β -diketone or a β -ketoester.
6. (Previously presented). The liquid oligomeric composition, according to claim 3, wherein said β -dicarbonyl has equivalent functionality (N) wherein $N = 2, 4, 6, \text{ or } 8$.
7. (Currently amended). The liquid oligomeric composition, according to claim 4, wherein a ratio of acceptor to donor functional groups is selected from the group consisting of $\geq 1:1$ where

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said β -dicarbonyl functionality=2, $\geq 4.5:1$ where said β -dicarbonyl functionality=6, and $\geq 3.5:1$ where said β -dicarbonyl functionality=8,

~~the molar acrylic functional group ratio of said diacrylate Michael acceptor to said β -dicarbonyl donor of functionality = 2 is $\geq 1:1$:~~

~~$\geq 1:1$ where said β -dicarbonyl functionality=2, ———~~

~~$\geq 4.5:1$ where said β -dicarbonyl functionality=4,~~

~~$\geq 4.5:1$ where said β -dicarbonyl functionality=6, and~~

~~$\geq 3.5:1$ where said β -dicarbonyl functionality=8.~~

8. (Currently amended). The liquid oligomeric composition, according to claim 4, wherein a ratio of acceptor to donor functional groups is selected from the group consisting of ≥ 2.1 where said β -dicarbonyl functionality=2, $\geq 6.4:1$ where said β -dicarbonyl functionality=4, $\geq 7.8:1$ where said β -dicarbonyl functionality=6, and $\geq 7.4:1$ where said β -dicarbonyl functionality=8.

~~the molar acrylic functional group ratio of said triacrylate Michael acceptor to said β -dicarbonyl donor is:~~

~~≥ 2.1 where said β -dicarbonyl functionality=2,~~

~~$\geq 6.4:1$ where said β -dicarbonyl functionality=4,~~

~~$\geq 7.8:1$ where said β -dicarbonyl functionality=6, and~~

~~$\geq 7.4:1$ where said β -dicarbonyl functionality=8.~~

9. (Currently amended). The liquid oligomeric composition, according to claim 4, wherein a ratio of acceptor to donor functional groups is selected from the group consisting of ≥ 3.3 where said acetoacetate functionality=2, $\geq 12.3:1$ where said β -dicarbonyl functionality=4, $\geq 13.2:1$ where said β -dicarbonyl functionality=6, and $\geq 12.7:1$ where said β -dicarbonyl functionality=8.

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~~the molar acrylic functional group ratio of said tetraacrylate Michael acceptor to said β -dicarbonyl donor is:~~

~~≥ 3.3 where said acetoacetate functionality=2,~~

~~$\geq 12.3:1$ where said β -dicarbonyl functionality=4,~~

~~$\geq 13.2:1$ where said β -dicarbonyl functionality=6, and~~

~~$\geq 12.7:1$ where said β -dicarbonyl functionality=8.~~

10. (Canceled).

11. (Previously presented). The liquid oligomeric composition, according to claim 1, wherein said mercaptan is a dimercaptan.

12. (Previously presented). The liquid oligomeric composition, according to claim 11, wherein said dimercaptan is selected from the group consisting of

ethylene glycol dimercaptopropionate,

diethylene glycol dimercaptopropionate,

4-t-butyl-1, 2-benzenedithiol,

bis-(2-mercaptoethyl) sulfide,

4, 4'-thiodibenzenethiol,

benzenedithiol,

glycol dimercaptoacetate,

glycol dimercaptopropionate ethylene bis (3-mercaptopropionate),

polyethylene glycol dimercaptoacetates,

polyethylene glycol di (3-mercaptopropionates),

2, 2-bis (mercaptomethyl)-1, 3-propanedithiol,

2, 5-dimercaptomethyl-1, 4-dithiane,

bisphenofluorene bis (ethoxy-3-mercaptopropionate),

4, 8-bis (mercaptomethyl)-3, 6, 9-trithia-1, 11-undecanedithiol,

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2-mercaptomethyl-2-methyl-1, 3-propanedithiol,
1, 8-dimercapto-3, 6-dioxaoctane, and
thioglycerol bismercapto-acetate.

13. (Previously presented). The liquid oligomeric composition, according to claim 11, wherein said di-functional mercaptan is ethylene glycol dimercaptopropionate.

14. (Previously presented). The liquid oligomeric composition, according to claim 1, wherein said mercaptan is a trimercaptan.

15. (Previously presented). The liquid oligomeric composition, according to claim 14, wherein said trimercaptan is selected from the group consisting of trimethylol propane (tris-mercaptopropionate) (TMPTMP), trimethylolpropane tris (3-mercaptopropionate), trimethylolpropane tris (3-mercaptoacetate), Tris-(3-mercaptopropyl) isocyanurate, 1, 2, 3-trimercaptopropane, dipentaerythritol, 1, 2, 4-trimercaptomethyl benzene, and tris(3-mercaptopropionate)triethyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione.

16. (Previously presented). The liquid oligomeric composition, according to claim 14, wherein said tri-functional mercaptan is trimethylol propane (tris-mercaptopropionate) (TMPTMP).

17. (Previously presented). The liquid oligomeric composition, according to claim 1, wherein said mercaptan is a polyfunctional mercaptan.

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18. (Previously presented). The liquid oligomeric composition, according to claim 17, wherein said polyfunctional mercaptan is selected from the group consisting of

Poly (mercaptopropyl methyl) siloxane (PMPMS),

4-mercaptomethyl-3, 6-dithia-1, 8-octanedithiolpentaerythritol tetrakis (3-mercaptoacetate), and pentaerythritol tetrakis (3-mercapto-propionate).

19. (Previously presented). The liquid oligomeric composition, according to claim 17, wherein said polyfunctional mercaptan is poly (mercaptopropyl methyl) siloxane (PMPMS).

20. (Previously presented). The liquid oligomeric composition, according to claim 1, wherein said Michael addition reaction is carried out in the presence of a strong base.

21. (Previously presented). The liquid oligomeric composition, according to claim 20, wherein said base is chosen from the group consisting of cyclic amidines, guanidines, group I alkoxides, quaternary hydroxides, quaternary alkoxides, and alkoxide bases generated in situ by reaction between a halide anion and an epoxy moiety.

22. (Previously presented). The liquid oligomeric composition, according to claim 20, wherein said base is chosen from the group consisting of diazabicycloundecene (DBU), diazabicyclononene (DBN), and 1,1,3,3-tetramethyl guanidine.

23. (Previously presented). The liquid oligomeric composition, according to claim 21, wherein said alkoxide is generated in-situ by reaction between a quaternary halide and an epoxide moiety.

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24. (Currently amended). The liquid oligomeric composition, according to claim 4, ~~wherein~~ said comprising a diacrylate ~~[[is]]~~ selected from the group consisting of:

ethylene glycol diacrylate, propylene glycol diacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, tetrapropylene glycol diacrylate, polyethylene glycol diacrylate, polypropylene glycol diacrylate, ethoxylated bisphenol A diacrylate,

bisphenol A diglycidyl ether diacrylate, resorcinol diglycidyl ether diacrylate, 1, 3-propanediol diacrylate, 1, 4-butanediol diacrylate, 1, 5-pentanediol diacrylate, 1, 6-hexanediol diacrylate, neopentyl glycol diacrylate, cyclohexane dimethanol diacrylate,

ethoxylated neopentyl glycol diacrylate, propoxylated neopentyl glycol diacrylate, ethoxylated cyclohexanedimethanol diacrylate, propoxylated cyclohexanedimethanol diacrylate, acrylated epoxy diacrylates, aryl urethane diacrylates, aliphatic urethane diacrylates, polyester diacrylates, and mixtures thereof.

25. (Currently amended). The liquid oligomeric composition, according to claim 4, ~~wherein~~ said comprising a triacrylate ~~[[is]]~~ selected from the group consisting of:

trimethylol propane triacrylate, glycerol triacrylate, ethoxylated trimethylolpropane triacrylate, propoxylated trimethylolpropane triacrylate, tris (2-hydroxyethyl) isocyanurate triacrylate, ethoxylated glycerol triacrylate, propoxylated glycerol triacrylate, pentaerythritol triacrylate, aryl urethane triacrylates, aliphatic urethane triacrylates, melamine triacrylates, aliphatic epoxy triacrylates, epoxy novolac triacrylates, polyester triacrylates and mixtures thereof.

26. (Currently amended). The liquid oligomeric composition, according to claim 4, ~~wherein~~ said comprising a tetraacrylate ~~[[is]]~~ selected from the group consisting of:

pentaerythritol tetraacrylate, ethoxylated pentaerythritol tetraacrylate, propoxylated pentaerythritol tetraacrylate, dipentaerythritol tetraacrylate, ethoxylated dipentaerythritol tetraacrylate, propoxylated dipentaerythritol tetraacrylate, aryl urethane tetraacrylates, aliphatic

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urethane tetraacrylates, melamine tetraacrylates, epoxy novolac tetraacrylates, and mixtures thereof.

27. (Previously presented). The liquid oligomeric composition, according to claim 6, wherein said comprising a β -dicarbonyl donor compound having functionality = 2 [[is]] selected from the group consisting of: ethyl acetoacetate, methyl acetoacetate, 2-ethylhexyl acetoacetate, lauryl acetoacetate, t-butyl acetoacetate, acetoacetanilide, N-alkyl acetoacetanilide, acetoacetamide, 2-acetoacetoxyethyl methacrylate, allyl acetoacetate, benzyl acetoacetate, 2, 4-pentanedione, 2, 4-hexanedione, 3, 5-heptanedione isobutyl acetoacetate, [[and]] 2-methoxyethyl acetoacetate, and mixtures thereof.

28. (Previously presented). The liquid oligomeric composition, according to claim 6, wherein said comprising a β -dicarbonyl donor compound having functionality = 4 [[is]] selected from the group consisting of: 1,4-butanediol diacetoacetate, 1,6-hexanediol diacetoacetate, neopentyl glycol diacetoacetate, cyclohexane dimethanol diacetoacetate, [[and]] alkoxyated bisphenol A diacetoacetate, and mixtures thereof.

29. (Previously presented). The liquid oligomeric composition, according to claim 6, wherein said comprising a β -dicarbonyl donor compound having functionality = 6 [[is]] selected from the group consisting of: trimethylol propane triacetoacetate, glycerin triacetoacetate, and polycaprolactone triacetoacetates, [[and]] alkoxyated derivatives thereof, and mixtures thereof.

30. (Previously presented). The liquid oligomeric composition, according to claim 6, wherein said comprising a β -dicarbonyl donor compound having functionality = 8 [[is]] selected from the group consisting of pentaerythritol tetraacetoacetate and alkoxyated derivatives thereof.

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31. (Previously presented). The liquid oligomeric composition, according to claim 2, wherein said Michael addition reaction occurs in the presence of at least one non-reactive solvent.

32. (Previously presented). The liquid oligomeric composition, according to claim 31, wherein said non-reactive solvent is selected from the group consisting of styrene, t-butyl styrene, α -methyl styrene, vinyl toluene, vinyl acetate, allyl acetate, allyl methacrylate, diallyl phthalate, C1 - C18-methacrylate esters, dimethacrylates, and trimethacrylates.

33. (Previously presented). The liquid oligomeric composition, according to claim 1, wherein said composition is shelf stable for more than one month and has residual pendant unsaturated acrylate groups.

34. (Previously presented). The liquid oligomeric composition, according to claim 1, further comprising a stabilizing agent.

35. (Previously presented). The liquid oligomeric composition, according to claim 34, wherein a preferred stabilizing agent comprises (N-nitroso-N-phenylhydroxylamine)3Al.

36. (Previously presented). The liquid oligomeric composition, according to claim 2, further comprising an acidifying agent.

37. (Previously presented). The liquid oligomeric composition, according to claim 36, wherein said acidifying agent is chosen from a group consisting of phosphoric acids, carboxylic acids, acid half esters, and inorganic acid esters.

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38. (Previously presented). The liquid oligomeric composition, according to claim 36, wherein a preferred acidifying agent is selected from the group consisting of phosphate esters of 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 4-hydroxybutyl acrylate, and 4-hydroxybutyl methacrylate.

39. (Previously presented). The liquid oligomeric composition, according to claim 2, further comprising a monoacrylate.

40. (Previously presented) The liquid oligomeric composition, according to claim 39, wherein said monoacrylate is chosen from the group consisting of $C_1 - C_{18}$ acrylate esters, isobornyl acrylate (IBOA), tetrahydrofurfuryl acrylate (THFFA), 2-(2-ethoxy ethoxy) ethyl acrylate (EOEOEA), phenoxyethyl acrylate (PEA), hydroxyalkyl acrylate, monoalkyl polyalkylene glycol acrylate, siloxane, silane or silicone acrylate, perfluoroalkyl acrylate, caprolactone acrylate, and mixtures thereof.

41. (Currently amended). The liquid oligomeric composition, according to claim 39, wherein said monoacrylate is present up to ~~about 0 to~~ about 50 mol %.

42. (Previously presented). The liquid oligomeric composition, according to claim 2, further comprising a free-radical generator.

43. (Previously presented). The liquid oligomeric composition, according to claim 42, wherein said free-radical generator comprises a peroxide.

44. (Previously presented). The liquid oligomeric composition, according to claim 43, wherein said peroxide is selected from the group consisting of methyl ethyl ketone peroxide (MEKP),

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tert-butyl perbenzoate (TBPB), cumyl peroxide, and t-butyl peroxide.

45. (Canceled).

46. (Currently amended). A polymerized product obtained by crosslinking:

a liquid oligomeric composition comprising:

a multifunctional mercaptan; [[and]]

an organic soluble, ungelled, uncrosslinked, Michael addition reaction product; and

the substantial total absence of exogenous photoinitiator, crosslinked in the presence of a free-radical-generator.

47. (Previously presented). The polymerized product, according to claim 46, wherein said free-radical generator is actinic light.

48. (Previously presented). The polymerized product, according to claim 46, wherein said free-radical generator is a peroxide.

49. (Canceled).

50. (Previously presented). A method of making a liquid oligomeric composition, wherein said oligomeric composition has pendant unsaturated acrylate groups, the method comprising:

reacting a multifunctional acrylate Michael acceptor and a β -dicarbonyl Michael donor in the presence of a strong base to form a Michael adduct having pendant unsaturated acrylate groups;

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adding an acidifying agent to said adduct in an amount at least stoichiometric with said base; and

admixing a multifunctional mercaptan.

51. (currently amended). A method of using a liquid oligomeric composition comprising:

providing a liquid oligomeric composition comprising:

a multifunctional mercaptan, and

an organic soluble, ungelled, uncrosslinked, Michael addition reaction product

having a plurality of pendant unsaturated acrylate groups;

applying said oligomeric composition to a surface; and

curing said composition in the ~~substantial~~ total absence of exogenous photoinitiator.

52. (Previously presented). A method of using a liquid oligomeric composition, according to claim 51, wherein curing comprises providing a free-radical generator.

53. (Previously presented). A method of using a liquid oligomeric composition, according to claim 52, wherein said free-radical generator is actinic light.

54. (Previously presented). A method of using a liquid oligomeric composition, according to claim 52, wherein curing comprises reacting said composition under base catalyzed conditions.

55. (Previously presented). A method of using a liquid oligomeric composition, according to claim 52, wherein said composition further comprises at least one additive.

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56. (Previously presented). A method of using a liquid oligomeric composition, according to claim 55, wherein said additive is selected from the group consisting of pigments, gloss modifiers, flow and leveling agents and other additive as appropriate to formulate coatings, paints, laminates, sealants, adhesives and inks.

57. (Currently amended). The liquid oligomeric composition, according to claim 39, wherein said monoacrylate is present ~~up to about~~ in amounts from greater than 0 to about 25 mol %.

58. (Currently amended). The liquid oligomeric composition, according to claim 39, wherein said monoacrylate is present ~~up to about~~ in amounts from greater than 0 up to about 12.5 mol %.